

**Computational Nanotechnology of Molecular Materials, Electronics, and Actuators with  
Carbon Nanotubes and Fullerenes**

Deepak Srivastava\*  
Computational Nanotechnology (CSC/NAS)  
NASA Ames Research Center, Moffett Field, CA 94035-1000

Madhu Menon  
Department of Physics and Center for Computational Sciences  
University of Kentucky, Lexington, KY 40506

Kyeongjae Cho  
Division of Mechanics and Computation, Department of Mechanical Engineering  
Stanford University, Stanford, CA 94305-4040

**Abstract:**

The role of computational nanotechnology in developing next generation of multifunctional materials, molecular scale electronic and computing devices, sensors, actuators and machines is described through a brief review of enabling computational techniques and few recent examples derived from computer simulations of carbon nanotube based molecular nanotechnology.

\* Author to whom correspondence should be addressed: [deepak@nas.nasa.gov](mailto:deepak@nas.nasa.gov)

## 1. Background:

During the 2<sup>nd</sup> half of the 20<sup>th</sup> century, we have experienced the microelectronics revolution that has started from the development of vacuum tube electronic computers (e.g., ENIAC in 1947) and has led to silicon-based integrated electronic devices. Current information technology (IT) has become only possible because of mature development in information processing technology (e.g., computers) and communication technology (e.g., optical and wireless networks). As the 21<sup>st</sup> century begins, the microelectronic device revolution is facing major obstacles in continuing the device scaling which has followed the famous Moore's law. The current VLSI devices are pushing the physical limits of electronic device materials. Insulating oxide layer thickness in next generation of transistors has become thinner than 2 nm leading to possibly direct tunneling of electrons, and the required dopant concentration in the channel region has begun to exceed the solubility limit of silicon. Currently, there is no clear solution to continue the device scaling beyond 2010, and the world of science and technology community is experiencing a transition of technology paradigm from the microdevice technology to an emerging new technology that is now widely known as *nanotechnology*.

The science and technology of nanoscale materials, devices and applications in areas such as materials, electronics, computers, sensors, actuators, and machines fall within the realm of nanotechnology. This definition is kept intentionally narrow to keep the focus on the 'revolutionary' field of nanotechnology that is pushing the boundaries in many enabling science and technology areas. For the purpose of this article, we consider atoms and molecules, or extended atomic or molecular structures, as the basic units or building blocks of fabricating future generations of electronics, materials, devices and applications. At nanometer length scales, in fact, many diverse enabling areas and associated technologies start to merge because these are derived from the similar materials properties of the molecular building blocks. It turns out that sometimes the same molecularly perfect structure that is responsible for exceptionally strong structural and mechanical behavior, in one class of applications of the system, is also responsible for the exotic electronic and chemical behavior in another class of applications. For example, in bio-nanotechnology, DNA molecular strands have attracted a number of intensive investigations spanning fields as diverse as self-assembling templates for bio-sensors and detectors, molecular electronics with metallic or semiconducting DNAs, and molecular building blocks for a wide

variety of biological materials. Similarly, among synthetic inorganic materials, there are fullerenes and/or carbon nanotubes that are well known for exceptionally strong and stiff mechanical properties as well as also the exotic electronic properties that are at least competitive or even better than any other conventional electronic material known so far.

The role of *computational* nanotechnology has become critically important in nanotechnology development because the length and time scales of important nanoscale systems and phenomenon have shrunk to the level where they can be directly addressed with computer simulations and theoretical modeling with very high accuracy. As a result of rapidly increasing computing power to perform large scale and high fidelity simulations, it is becoming increasingly possible for the nanoscale simulations to be also predictive in nature. Computational nanotechnology is emerging as a fundamental engineering analysis tool for novel nanodevice design in a similar way that the continuum finite element analysis (FEA) was and has been used for design and analysis of most of the current generation of engineering systems (e.g., automobiles, ships, airplanes, MEMS devices, and ICs).

The main objective of this article is to introduce, to the general reader, about the possibilities that can be explored with computational nanotechnology and also to give a glimpse of possible technologies in the basic core areas of nanotechnology where major progresses are going to be made in the future. The selected core areas are molecular scale ultra-light weight extremely strong functional or smart materials, molecular scale or nanoscale electronics with possibilities of quantum computing, molecular scale sensors or actuators, and molecular machines or motors with synthetic materials. The underlying molecular scale building block in all the above four areas are fullerenes and carbon nanotube based molecular materials. It is only the different aspects of the physical, chemical, mechanical and electronic properties that have given rise to the diverse applications of this same material in a variety of the vastly different areas. The computational techniques needed to address the vastly different length scales, ranging from the materials and mechanical properties to the chemical and electronic properties of nanodevices, also differ in nature. In the first case, the detailed electronic behavior is not important while in the second case the electronic behavior may be essential to describe the relevant physical or chemical behaviors of the systems and the resulting applications.

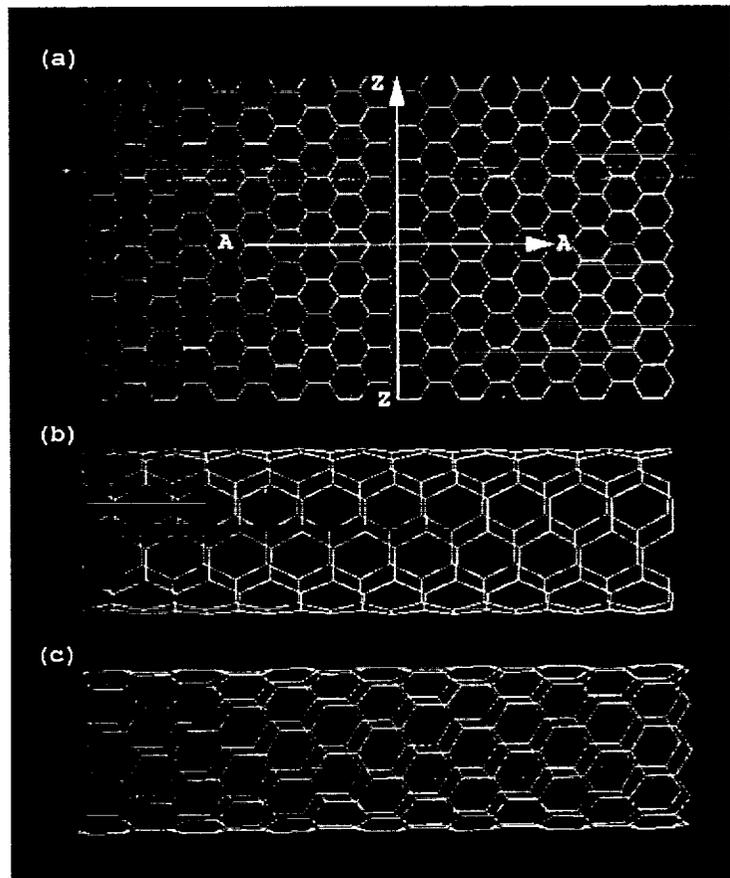
Finally, before getting into the details of computational techniques and nanodevice designs and applications, it is worthwhile to take a side step and answer the question of “what are fullerenes and carbon nanotubes?”

### 1.A. Nanotubes and Fullerenes as Building Blocks of Nanodevices

Fullerenes are close-caged molecules containing only hexagonal and pentagonal interatomic bonding networks, and nanotubes are large linear fullerenes with aspect ratios as large as  $10^3$ - $10^5$ . Since their discovery about 10 years ago [1-3], carbon nanotubes (and many derivatives of fullerenes, such as nanocones, nanosprings, and nano toruses) have been extensively investigated by both experimental and theoretical means. [4] Even though many nanoscale fullerene materials (which are made entirely of carbon atoms) are observed regularly in experiments, a controlled production in large quantities of fullerenes and nanotubes with well-defined characteristics has not been completely worked out yet.

A single-wall carbon nanotube (SWNT) is best described as a rolled-up shell of graphene sheet [Fig.1a] which is made

of benzene-type hexagonal carbon rings. The ends of the graphene shell in a nanotube are capped by half-fullerenes, and unlike graphene, fullerenes are made of a combination of hexagons and pentagons to satisfy the Euler's rule governing the number of pentagons in any closed cage



**Figure 1** (a) A graphene sheet made of C atoms placed at the corners of hexagons forming the lattice with arrows AA and ZZ denoting the rolling direction of the sheet to make (b) an (5,5) armchair and (c) a (10,0) zigzag nanotubes, respectively.

structures. Multi-wall nanotubes (MWNTs) are more common and can be produced in bulk with current experimental techniques. A multi-wall nanotube is rolled-up stack of graphene sheets into concentric SWNTs, with the ends again capped by half-fullerenes. The nomenclature  $(n,m)$  used to identify each single-wall nanotube refers to integer indices of two graphene unit lattice vectors corresponding to the chiral vector of a nanotube. [4] Chiral vectors determine the directions along which the graphene sheets are rolled to form shell structures and perpendicular to the tube axis vectors as explained in Ref. 4. The nanotubes of type  $(n,n)$ , as shown in Figure 1b, are commonly called armchair nanotubes because of the  $\backslash/\backslash/$  shape, perpendicular to the tube axis, and have a symmetry along the tube axis with a short unit cell (0.25 nm) that can be repeated to make the entire section of a long nanotube. Another nanotubes of type  $(n,0)$  are known as zigzag nanotubes (Fig 1c) because of the  $\wedge$  shape and also have a short unit cell (0.43 nm) along the tube axis. All the remaining nanotubes are known as chiral nanotubes and have longer unit cell sizes along the tube axis. Details of the symmetry properties of the nanotubes and how to roll a sheet to make nanotubes of different chiralities are explained in Ref. 4.

The single and multi-wall nanotubes are interesting nanoscale materials for the following three reasons:

- A single-wall nanotube can be either metallic or semiconducting, depending on its chiral vector  $(n,m)$ , where  $n$  and  $m$  are two integers. The rule is that when the difference  $n-m$  is a multiple of three a metallic nanotube is obtained. If the difference is not a multiple of three a semiconducting nanotube is obtained. In addition it is also possible to connect nanotubes with different chiralities creating nanotube hetero-junctions, and these junctions can form a variety of nanoscale molecular electronic device components.
- Single and multi-wall nanotubes have very good elastomechanical properties because the two dimensional arrangement of carbon atoms in a graphene lattice allows large out-of-plane distortions, while the strength of carbon-carbon in-plane bonds keeps the graphene sheet exceptionally strong against any in-plane fracture or distortion. All distortions induced in a simulation or observed in static snapshot of experiments appear to indicate high

- elasticity of the nanotubes and point towards their possible use as a lightweight, highly elastic, and very strong fibrous material.
- Since nanotubes are hollow, tubular, caged molecules they have been proposed as lightweight large surface area packing material for gas-storage and hydrocarbon fuel storage devices, as well as nanoscale containers for molecular drug-delivery and casting structures for making nanowires and nanocapsulates.

A broad interest in nanotubes derives from the possibilities of a variety of applications in all of the above three technologically interesting areas. The nanotube hetero-junctions with electronic switching properties can be used for developing next-generation of computer components. Nanotubes with exceptionally stiff and strong mechanical properties can be used for making future generation lightweight structural components. Nanotubes as capsules can be used for storing and carrying hydrogen and other hydrocarbon based fuel in automobiles and or aboard a spacecraft.

It is also worth noting that carbon based materials are ideally suitable as molecular level building blocks for nanoscale systems design, fabrication and applications. From a structural or functional materials perspective carbon is the only element that exists in a variety of shapes and forms with varying physical and chemical properties. For example, diamond and layered graphite forms of carbon are well known, but the same carbon also exists also in planar sheet, rolled up tubular, coiled spring, rectangular hollow box, and nano conical forms. All basic shapes and forms needed to build any complex molecular scale architectures thus are already available with carbon. Additionally, by coating any carbon based nanoscale devices and applications with biological lipid layers and/or protein molecules it may be possible to extend in to the rapidly expanding area of bio-nanotechnology.

In the following, we discuss how the basic computational techniques in materials physics and chemistry (e.g., classical molecular dynamics, quantum molecular dynamics, ab-initio electronic structure methods, and quantum conductance at nanoscale) have resulted in predictive simulations of futuristic molecular scale materials, electronics, computers, sensors, and machines.

## **2. Shrinking of Length Scales: Computational Techniques for Nanoscale Simulations**

Until about 40 years ago, the computation of the thermodynamic properties of interacting, bulk condensed matter systems was carried out with analytical approximation methods for an infinite system. These analytical methods (e.g., virial expansion, Mayer expansion, etc.) were valid only in the dilute system limit, and the approximations still had to be carried out numerically beyond a few orders. Since then, a new kind of approximation scheme, namely, exact numerical computation of the properties of a finite sample system, has become the most common approach to the study of interacting condensed matter systems. Molecular dynamics (MD) refers most commonly to the situation where the motion of atoms or molecules is treated in approximate finite difference equations of Newtonian mechanics. Except when dealing with very light atoms and very low temperatures, the use of classical mechanics is well justified.

Until about two decades ago, MD computations primarily used simplistic pair potentials (e.g., Lennard-Jones, Born-Mayer) to describe inert gases in condensed phase systems or the materials that tend to form hexagonal closed packing structures. A slow transition to describe dynamics of more complex condensed phase systems such as metals and semiconductors with explicit or implicit many-body force field functions began with Embedded Atom Method (EAM) type potentials for metals, [5] and Stillinger-Weber (SW) [6] and/or Tersoff-Brenner (TB) [7, 8] type potentials for semiconductors. [9] Based on the variations of these EAM and SW/TB type potentials, a wide variety of force field functions have been proposed and used in classical molecular dynamics simulations. Many of the potentials are expected to work well in the regimes of physical parameters in which they were constructed in the first place. The EAM type potentials for metals and SW or TB type potentials for semiconductors have been used in a wide variety of scenarios for which they were constructed for, and have given fairly good results in agreement with the expectation. However, currently, there is no universal classical force field function that works for all materials and in all scenarios. Consequently, one needs to be careful specially for the description of dynamics or reactions with surfaces and clusters where true chemical changes (involving electronic rearrangements) with large atomic displacements are expected to occur.

In recent years several more accurate quantum molecular dynamics schemes have been developed in which the forces between atoms are computed at each time step via quantum mechanical calculations within the Born-Oppenheimer approximation. The dynamic motion for ionic positions are still governed by Newtonian or Hamiltonian mechanics, and described by molecular dynamics. The most widely known and accurate scheme is the Car-Parrinello (CP) molecular dynamic method [10], where the electronic states and atomic forces are described using the *ab-initio* density functional method (usually within the local density approximation (LDA)). While such *ab-initio* MD simulations can now be performed for systems consisting of a few hundred atoms, there is still a vast range of system sizes for which such calculations start to stretch the limits of present day computational resources and become intractable. In the intermediate regimes, between large scale classical MD and quantum (CP) dynamics methods, semi-empirical quantum simulation approaches cover an important system size range where classical potentials are not accurate enough and *ab-initio* computations are not feasible. The tight-binding molecular dynamics (TBMD) [11] approach thus provides an important bridge between the accurate *ab-initio* quantum MD and classical MD methods.

In computational nanotechnology research, these three simulation methods can be used in a complimentary manner to improve the computational accuracy and efficiency. Based on experimental observations or theoretical dynamic and structure simulations, the atomic structure of a nanosystem can first be investigated. After the nanoscale system configurations have been finalized, the electronic behaviors of the system are investigated through static *ab-initio* electronic energy minimization schemes [12] or through studies of quantum conductance [13] behavior of the system. The *ab-initio* electronic structure investigations provide highly accurate information not only about the thermodynamic minimum energy configurations of the system, but also about the chemical reactions and charge transfers that occur when two nanoscale systems are brought together or taken apart. Studies of the transport behavior, finally, are important in designing the nanodevices where the operating characteristics are usually determined by the electronic, thermal, acoustic or chemical signal transfer through the system.

The inclusion of "all the possible" simulation and computational techniques, as the enabling technologies for the computational nanotechnology, is too broad to be covered in a comprehensive

manner within the scope of this article. In the following, therefore, we briefly discuss some of the main computational techniques. For example, classical molecular dynamics, tight-binding molecular dynamics, ab-initio electronic structure, and quantum electronic transport are the computational methods that we have specifically used to investigate the applications in molecular materials, electronics, quantum computer, sensors, and machines, as discussed later in this article. In an idealized scenario for the future of computational nanotechnology, one would think of an interactive 'virtual reality' problem solving environment (PSE) where all of the above mentioned schemes and techniques are implemented as a multiscale Nano-CAD simulator for nanoscale system simulations. Such interactive virtual reality PSE simulators will do for the new nanotechnology systems developments and implementation what computer aided design (CAD) simulators, based on FEA, have done for the present day engineering applications.

## 2. A. Classical Molecular Dynamics:

The classical molecular dynamics describes the atomic scale dynamics of a system where atoms and molecules move while simultaneously interacting with many of the other atoms and molecules in the vicinity within a cut-off distance. The dynamic evolution of the system is governed by Newton's or Hamilton's classical equations of motion,  $d^2\mathbf{R}_i/dt^2 = \mathbf{F}_i = -dV/d\mathbf{R}_i$ , which is derived from the classical Hamiltonian of the system,  $H = \sum \mathbf{P}_i^2/2M_i + V(\{\mathbf{R}_i\})$ . [14] As we will show in the following section, each atom moves and acts simply as a particle that is moving in the many-body force-field of the other similar particles,  $V(\{\mathbf{R}_i\})$ , which can be obtained from more accurate quantum simulations. The atomic and molecular interactions, describing the dynamics, thus are given by classical many-body force field functions, and the atomic interaction energy function  $V(\{\mathbf{R}_i\})$  can be written in terms of pair and many-body interactions depending on the relative distances among different atoms. [5-8] The atomic forces are derived as analytic derivatives of the interaction energy functions,  $\mathbf{F}_i(\{\mathbf{R}_i\}) = -dV/d\mathbf{R}_i$ , and are used to construct Hamilton's classical equations of motion which are 2<sup>nd</sup> order ordinary differential equations. These equations are approximated as finite difference equations with discrete time step  $\Delta t$  and are solved by the standard Gear's 5th order Predictor-Corrector or Verlet's leap-frog methods. The simulations can be performed under a variety of thermodynamic equilibrium or non-equilibrium conditions, [14] and,

depending on the force field function used, can describe reactions between atoms and molecules as the molecular building blocks approach each other.

In its global structure, our general MD code is typically implemented using a more-or-less conventional molecular-dynamics algorithm, i.e., an algorithm to find a numerical solution of a set of coupled first-order ordinary differential equations given by the Hamiltonian formulation of Newton's Second Law. The MD code is applied to a collection of atoms with well-defined potential-energy functions, and the equations of motion are numerically integrated forward in finite time steps using a predictor-corrector method. We have used Tersoff-Brenner many-body potential to describe atomic interactions in hydrogen and carbon based systems for computational descriptions of carbon nanotubes, and Tersoff potential for mixed Si/Ge/C based systems. [7, 8] A major distinguishing feature of the Tersoff-Brenner potential is that short-range bonded interactions are reactive so that chemical bonds can form and break during the course of a simulation. Therefore, compared to some other molecular dynamics codes, the neighbor list describing the environment of each atom includes only a few atoms and needs to be updated more frequently. The computational cost of the many-body bonded interactions is relatively high compared to the cost of similar methods with non-reactive interactions with simpler functional forms. As a result, the overall computational costs of both short-range interactions and long-range, non-bonding van der Waals (Lennard Jones 6-12) interactions are roughly comparable.

For large scale atomistic modeling ( $10^5$ - $10^8$  atoms), multiple processors are used for MD simulations, and the MD code needs to be parallelized. A route to the parallelization of a standard MD code involves decoupling of the neighbor list construction from the computation of the atomic forces, and parallelizing each part in the most efficient way possible. Parallelization of the MD code using Tersoff-Brenner potential for carbon atom interactions was attempted and achieved recently. An example of the parallel implementation of this classical MD code is described in detail elsewhere. [15] The parallelized MD code has been utilized in simulations of mechanical response properties of the nanotubes, nanotube-polymer composites, mechanical strain driven chemistry of carbon nanotubes, and molecular gears and motors powered by laser fields. Some of these applications are described below.

## 2.B. Generalized Tight-binding Molecular Dynamics:

In the most general approach of full quantum mechanical description of materials, atoms are described as a collection of quantum mechanical particles, nuclei and electrons, governed by the Schrodinger equation,  $H \Phi[\{\mathbf{R}_I, \mathbf{r}_i\}] = E_{\text{tot}} \Phi[\{\mathbf{R}_I, \mathbf{r}_i\}]$ , with the full quantum many-body Hamiltonian operator  $H = \sum \mathbf{P}_I^2 / 2M_I + \sum Z_I Z_J e^2 / R_{IJ} + \sum \mathbf{p}_i^2 / 2m_e + \sum e^2 / r_{ij} - \sum Z_I e^2 / |\mathbf{R}_I - \mathbf{r}_i|$ , where  $\mathbf{R}_I$  and  $\mathbf{r}_i$  are nuclei and electron coordinates. Using the Born-Oppenheimer approximation, the electronic degrees of freedom are assumed to follow adiabatically the corresponding nuclear positions and the nuclei coordinates become classical variables. With this approximation, the full quantum many-body problem is reduced to a quantum many-electron problem  $H[\mathbf{R}_I] \Psi[\mathbf{r}_i] = E_e \Psi[\mathbf{r}_i]$ , where  $H = \sum \mathbf{P}_I^2 / 2M_I + H[\mathbf{R}_I]$ .

In the tight-binding model, [11] an approximation is made to further simplify the quantum many-electron problem. It is assumed that the crystal potential is strong, which is the same as assuming that the ionic potentials are strong so that when an electron is captured by an ion during its motion through the lattice, the electron remains at that site for a long time before leaking, or tunneling, to the next ion site. During the capture interval, the electron orbits primarily around a single ion uninfluenced by other atoms so that its state function is essentially that of an atomic orbital. Most of the time the electron is tightly bound to its own atom. In other words, the atomic orbital is modified only slightly by the other atoms in the solid.

The tight-binding wave function is, therefore, constructed by taking a linear combination of localized atomic orbitals, modulated by a Bloch wave function phase factor for a periodic lattice. This ensures that an electron in a tight-binding level will be found, with equal probability, in any cell of the crystal, since its wave function changes only by the phase factor as one moves from one cell to another. The computational efficiency of the tight-binding method derives from the fact that the Hamiltonian  $H[\mathbf{R}_I]$  can be parameterized. Furthermore, the electronic structure information can be easily extracted from the tight-binding Hamiltonian, which in addition also contains the effects of angular forces in a natural way.

Harrison [11] has attempted to provide a minimal tight-binding theory with only 4 parameters (in addition to 4 dimensionless universal constants) that could describe qualitatively a wide range of materials and properties. While the focus of his work was tetrahedral solids, in later work with van Schilfgaard [16] he emphasized the necessity of including the nonorthogonality of the local environment in multicoordinated structures. This important factor has been generally overlooked by those seeking a transferable scheme. In our generalized tight-binding molecular dynamics (TBMD) calculations we employ a *non-orthogonal* tight-binding scheme proposed by Menon and Subbaswami with minimal number of adjustable parameters resulting in a transferable scheme applicable to clusters as well as bulk systems containing Si, C, B, N and H [17,18].

The generalized TBMD approach has been applied to variety of clusters, surfaces, nanotubes, fullerenes, and bulk carbon and silicon based materials. The main advantage of our generalized TBMD method is that it can be used to find an energy minimized structure of a nanoscale system under consideration without symmetry constraints. It turns out that sometimes symmetry-unconstrained dynamic energy minimization of a system helps in finding the global energetic minimum of the system which is not easily conceptualized on the symmetry consideration alone. Additionally, this method has been found to be very accurate in describing the chemical reactions between the intermediate size systems because the atomic forces are set to their natural cutoff, i.e., where the electronic interactions between the reacting species have decayed appreciably, rather than the imposed short range cutoff used in many-body potentials employed in classical MD simulations. The parallelization of the TBMD code involves parallelization of the direct diagonalization (of the electronic Hamiltonian matrix) part as well as the parallelization of the MD part. The parallelization of a sparse symmetric matrix giving many eigen values and eigen vectors is a complex bottle neck in the simulation of large intermediate range system and needs development of new algorithms for this specific purpose.

### **2.C. *Ab-initio* Simulation Methods:**

*Ab initio* or first principles method is a simulation method to solve complex quantum many-body Schroedinger equation using numerical algorithms. [12, 19] Tight binding (TB) method described in the previous section is another quantum mechanical simulation method based on the linear combination of atomic orbital (LCAO) approximation to describe the quantum mechanical electronic wave functions. Because of the simple basis expansion using atomic orbitals, TB method

is generally about 1000 times more efficient than *ab-initio* method. However, *ab-initio* method provides more accurate description of quantum mechanical behavior of materials properties even though the system size is currently limited to about few hundred atoms. From this viewpoint, MD, TB, and *ab-initio* methods form a complimentary set of simulation tools to study diverse atomic scale processes in nanodevice modeling.

Current *ab-initio* simulation methods are based on a rigorous mathematical foundation provided by two important works of Hohenberg and Kohn (1963) [20] and Kohn and Sham (1964). [21] Hohenberg and Kohn have proved a theorem that the ground state energy ( $E_{el}$ ) of many-electron system is a functional of total electron density,  $\rho(\mathbf{r})$ , rather than the full electron wave function,  $\Psi[\mathbf{r}_i]$ :  $E_{el}(\Psi[\mathbf{r}_i]) \equiv E_{el}(\rho(\mathbf{r}))$ . The Hamiltonian operator  $H$  and Schrodinger equation are given by

$$H[\mathbf{R}_I] = \sum \mathbf{p}_i^2/2m_e + \sum e^2/r_{ij} - \sum Z_I e^2/|\mathbf{R}_I - \mathbf{r}_i| + \sum Z_I Z_J e^2/R_{IJ},$$

$$H[\mathbf{R}_I]\Psi[\mathbf{r}_i] = E_{el} \Psi[\mathbf{r}_i],$$

where  $\{\mathbf{R}_I\}$  and  $\{\mathbf{r}_i\}$  are atomic positions and electronic coordinates. The density functional theory (DFT) is derived from the fact that the ground state total electronic energy is a functional of the density of the system. Subsequently, Kohn and Sham have shown that the DFT can be reformulated as single electron problem with self-consistent effective potential including all the exchange-correlation effects of electronics interactions:

$$H_1 = \mathbf{p}^2/2m_e + V_H(\mathbf{r}) + V_{xc}[\rho(\mathbf{r})] + V_{ion-el}(\mathbf{r}),$$

$$H_1 \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad i = 1, \dots, N_{tot},$$

$$\rho(\mathbf{r}) = \sum |\psi_i(\mathbf{r})|^2.$$

This single electron Schrodinger equation is known as Kohn-Sham equation, and the local density approximation (LDA) has been introduced to approximate the unknown effective exchange-correlation potential. This DFT-LDA method has been very successful in predicting materials properties without using any experimental inputs other than the identity of the constituent atoms.

For practical applications the DFT-LDA method has been implemented with a pseudopotential approximation and a plane wave (PW) basis expansion of single electron wave functions. [12,19] These systematic approximations reduce the electronic structure problem as a self-consistent matrix diagonalization problem. Over the last three decades, the simulation method has been rapidly improved from iterative diagonalization (ID) method to Car-Parrinello molecular dynamics (CPMD) [10] to conjugate gradient (CG) minimization method. CPMD has significantly improved the computational efficiency by reducing the  $N^3$  scaling of ID method down to  $N^2$  scaling. The CG method has further improved the efficiency by an additional factor of 2-3. [12,19] One of the popular DFT simulation programs is Vienna Ab initio Simulation Package (VASP) which is available through a license agreement.[22] Another useful DFT simulation program has been developed in C++ language.[23] In addition to these simulation programs, there is also a commercial package from Molecular Simulation Inc. With these and other widely used DFT simulation packages, the *ab-initio* simulation method has been established as a major computational materials research tool .

## **2.D. Quantum Conductance in Nanoscale Systems:**

Quantum conductance can be calculated as a generalization of the transmission amplitude  $T(E)$  of an incident electron with energy  $E$  in simple one dimensional potential barrier problem. The Landauer expression is generally used to obtain quantum conductance from the transmission function  $T(E)$  as a function of the injected electron energy. [24] The transmission function is obtained using the Green's function formalism that has been described in detail recently. [13] In the nanotube devices under current consideration, a connection to the outside world is made through metallic leads. A realistic treatment of a nanotube interaction with metal electrodes must involve a judicious construction of the Green's function and is an involved process. To maintain a consistency in the simulations, it is proper to use the tight-binding (TB) formulation for both the Hamiltonian and the Green's function. The TB Hamiltonian described above consists of  $N$  by  $N$  matrices, where  $N = N(\text{at}) \times N(\text{orb})$ ,  $N(\text{at})$  is the number of atoms in the embedding subspace, and  $N(\text{orb})$  is the number of orbitals on each atom. Contrary to previous theoretical works on quantum transport which use  $N(\text{orb}) = 1$  (only one pi-electron orbital per atom), for accuracy, we use  $N(\text{orb}) = 9$  that includes 1s, 3p and 5d orbitals for C and Ni (a representative material for metal leads) interface, and  $N(\text{orb}) = 4$  for C atoms. This Hamiltonian has been used with success in the

treatment of transition metal systems as well as their interactions with carbon fullerenes and nanotubes [25,26].

We have used the same TB Hamiltonian to perform full symmetry unconstrained molecular dynamics relaxations for the SWNT systems. Consideration of the atomic relaxation is essential and has shown to give results significantly different from the cases where dynamic relaxation was not allowed. In addition, the quantum conductance simulations are generally complemented by the *ab-initio* calculations of the electronic density of states or the energy differences between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) states because features observed in the conductance are generally explained by the qualitative movements of the density of states or HOMO (LUMO) states with respect to the Fermi level of the system.

For a calculation of quantum conductivity, the Green's function formalism is used to embed a nanotube between host lattices consisting of transition metal atoms forming the semi-infinite leads at the two ends. [27] A boundary surface  $S$  separates the embedded system (tube) from the host lattice (leads) with the Green's function of the host satisfying the Dirichlet's boundary condition on  $S$ . [28] The lead-tube interaction is incorporated through the introduction of an electron self-energy term in the formalism. There are two self-energy terms, one for each metal-lead. Although it is desirable to have the calculations performed self-consistently, the size of the system (number of atoms as well as the use of many orbitals for each atom) makes this prohibitively expensive. Previous self-consistent calculations of quantum conductance have involved only very small size systems (typically less than 15 atoms). [29] The novel features of the current method are that the Hamiltonian used in calculating the conductivity is identical to the one used in performing tight-binding molecular dynamics simulations for relaxing all structures considered.

### **3. Applications in a Nano-World**

In this section we describe several representative examples where computational nanotechnology has clearly played an important role in either explaining some recent experimental observations, or predicting structures (or properties) which have been later fabricated (or measured) in experiments. For examples, on the one hand the driving atomistic mechanism of experimentally observed local collapse of axially compressed thin carbon nanotubes is explained recently by our tight-binding

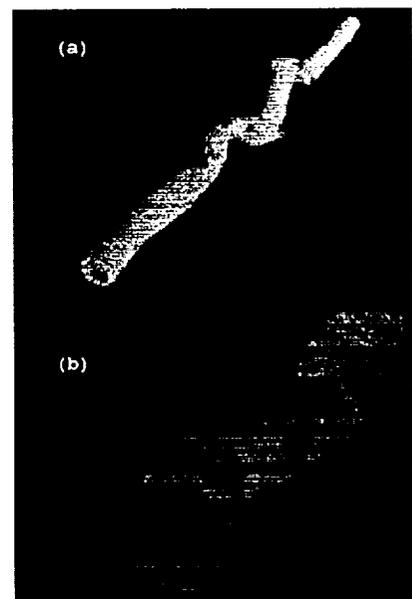
quantum molecular dynamics simulations, and on the other hand our predicted multi-terminal carbon nanotube heterojunctions, as molecular electronic devices, are now fabricated in experiments and measured for electronic transport properties. Additionally, we also include some more recent predicted structures and phenomena that are yet to be made and measured in experiments, as well as are yet to be exploited in future nanotechnology applications.

The areas covered are light-weight high-strength multifunctional materials, nanotube heterojunctions for molecular electronics, doped fullerenes and diamond nanocrystallite for fabrication of solid-state quantum bits, and interactions of gas molecules with nanotubes (electro mechanical coupling of nanotubes) for chemical sensor (mechanical sensor/actuator) applications.

### 3. A. Nanomechanics of C and BN Nanotubes: Nanostructured 'Skin-Effect'

Since their discovery in 1991, [1-3] the single- and multi-wall carbon nanotubes (CNT) have been shown to have exceptionally strong and stiff mechanical characteristics along the axis of the tube, and very flexible characteristics along normal to the axis of the tube. [30-34] For axial deformations, the Young's modulus of the single-wall CNTs can reach beyond 1 TPa, and the yield strength can be as large as 120 GPa. Some efforts have been recently made to take advantage of the nanotube strengths as reinforcing fibers in nanotube-polymer composite materials. [35-38]

The initial investigations, using classical molecular dynamics simulations with Tersoff-Brenner potential, showed that the tubes are extremely stiff under axial compression, and that the system remains within elastic limit even for very large deformations (up to 15% strain). [15, 30, 31] Nonlinear elastic instabilities, with the appearance of 'fins' like structures, are observed during these deformations, but the system remains within elastic limit and returns to the original unstrained state as soon as external constraining forces are removed. As shown in Fig. 2 when compressed beyond elastic limits, the single and multi-wall nanotubes undergo sideway bucklings, and plastic deformations occur mainly through

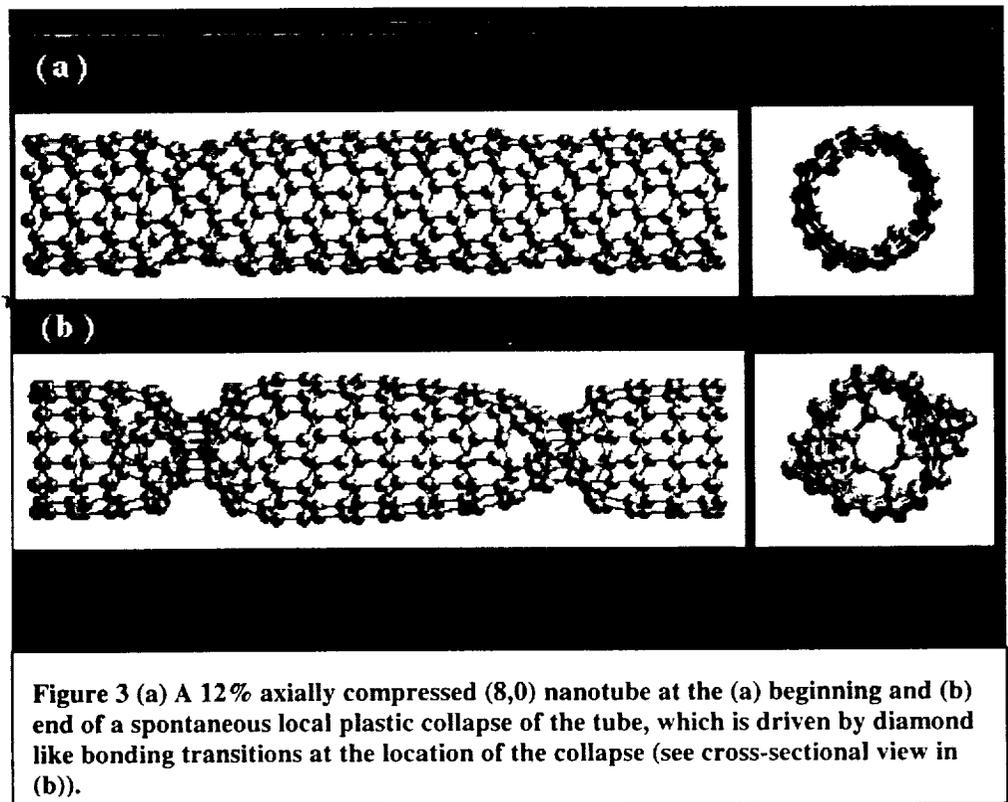


**Figure 2 Axial compression and plastic collapse of single- and multi-wall C nanotubes, simulated by classical MD method, shows garden hose**

extreme bending situations in the sideway buckled tubes. The red colored regions in the sideways buckled tubes are the regions under extreme stress. The garden-hose type sideway bucklings of thick multi-wall nanotubes have been also observed in TEM microscope images of nanotubes embedded in polymer composite materials. [36] However, another mode of deformations - plastic collapses or fractures of thin nanotubes without any buckling - was observed in experiments, [36] but these deformations have never been seen in any classical MD simulations with Tersoff-Brenner potential. [15,30,31]

To explain this discrepancy between the classical MD simulation results and the experimental observations, the simulations were repeated with more accurate quantum generalized tight-binding

molecular dynamics (GTBMD) description of nanotube nano-mechanics.[32] For an (8,0) carbon nanotube, within low values of compressive strain (less than 8% strain), the classical MD results are found to be in a reasonably good agreement with the quantum simulation results. Significant

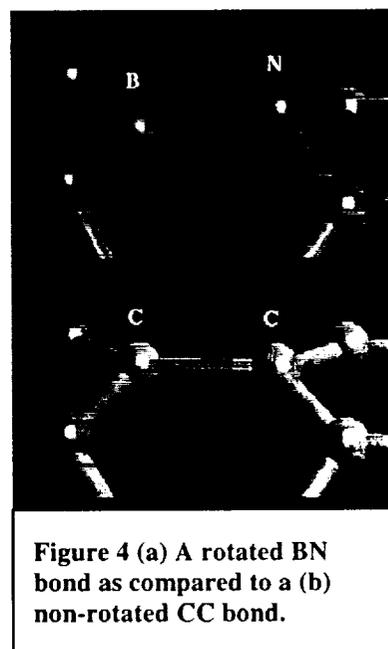


differences, however, start to occur for compressive strain larger larger than 8%. At 12% strain, as shown in Fig.3a, the structural deformation occurs asymmetrically near the two rigidly held ends with small changes in an otherwise circular cross-section of the tube. Strain relaxation in the center (highly strained) region of the tube drives the atoms, at the locations of the deformations, to gradually collapse inward as shown in Fig. 3b. Four-fold coordinated diamond-like bonds are

formed, and the structure is further 'pulled' inwards by the newly formed sp<sup>3</sup> type bonds (Fig. 3b cross-sectional view).

The energetics of the spontaneous inward collapse shows that there is a net energy release during the collapse process, and any local activation energy barrier for this transition is overcome by large release of strain energy (about 50 eV) in the uncollapsed center section since the sp<sup>3</sup> bonded carbon atoms form compact diamond structure with significantly reduced volume at the location of the collapse. The released strain energy of the uncollapsed section is dissipated in the form of heat and is removed by the GTBMD energy minimization process. In summary, a *novel* nano-plastic mechanism of compressed nanotubes is found and the mechanism is driven by graphitic to diamond like bonding transitions at the location of the collapse. [32] This is also reminiscent of a similar transition observed in the core of electron-beam irradiated and annealed bucky onions where graphitic core layers are converted to diamond at the generated high pressure (approximately 150 G Pa) on the core layers. [39] In our case, the similar mechanism is driven by the release of large amount of the accumulated strain in the un-collapsed section through structural relaxation, and the computed critical stress (about 153 G Pa for 12% compressed tube) is also in good agreement with the above value, [39] and also with the experimental estimations of the values reported by Lourie et. al., for the plastic collapse of thin nanotubes. [36]

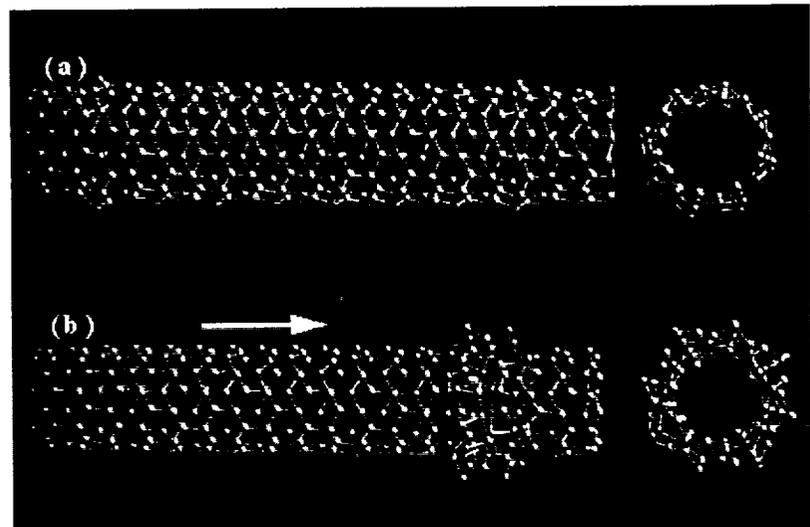
Similar simulations and analysis of axial compression of Boron-Nitride (BN) nanotubes have also been carried out. This study involves more variations in the physics and chemistry of the system involved, and has led us to predict a novel *anisotropic* compressibility of BN nanotubes. The main differences are due to two prominent structural differences between C and BN nanotubes. [40-42] (i) *Bond frustration effect*: Presence of B-B and N-N bonds in BN nanotubes makes them structurally unstable since they are energetically unfavorable. [40,42] (ii) *Bond rotation effect*: Structural relaxation causes each BN bond to be slightly rotated w.r.t. tube axis such that each N is rotated out and B is rotated into the surface of a BN nanotube. [Fig. 4] Based on the bond-



frustration effect, we have predicted that the zigzag BN nanotubes are more stable and can be easily made in experiments.[42] Recent experiments have indeed confirmed our prediction, and zigzag arrangement has been found to dominate BN nanotubes made in experiments. [43, 44]

The main effect of rotated BN bonds on the nanomechanics is to give an anisotropic mechanochemical characteristics to zigzag BN nanotubes. Since the BN bonds are aligned parallel to the tube axis in zigzag nanotubes, the strained BN bonds show a novel anisotropic plastic collapse under axial compression. In Fig. 5a, the surface of a BN nanotube with 14.5% compression shows a localized saw-tooth or "rippled" structure in which the B atoms have further rotated inward whereas the N atoms have further moved outward. [42] The spontaneous relaxation

of the structure (shown in Fig. 5a) leads to a plastic deformation or collapse, however, with an anisotropy only towards the right end of the compressed tube. (Fig. 5b) This anisotropy is driven by a strain release that occurs preferentially towards N atoms as the leading side of rotated BN bonds. [45] This anisotropic process is facilitated by a correlated "sliding" of N atoms further outward and B atoms



**Figure 5 (a) An (8,0) BN nanotube axially compressed by 14.5% strain (a) before, and (b) after the anisotropic plastic collapse where the excess strain has been released to the right.**

further inward. From a physical perspective, the outward sliding of N atoms is energetically favorable as it tends to reduce the strain due to the curvature of the tube, and the inward sliding of B atoms is less favorable as it tends to increase the curvature induced strains in the system. Furthermore, from a chemical perspective, the "repulsion" between neighboring B atoms moving inward is also energetically unfavorable. The anisotropic strain release and plastic deformation of the axially compressed BN nanotube is therefore driven by both physical and chemical considerations. [45]

Based on the anisotropic strain release and the resulting plastic deformation mechanism, *a hypothetical composite material reinforced by parallelly aligned zigzag BN nanotubes can be proposed*. The proposed material will exhibit a *nanostructured "skin" effect* in the sense that the material will have an anisotropic response to external axial strains. When subjected to large external axial strains, the material will react by minimizing the damage to the inner core side, while transferring all the damage to the outer "skin" or surface side. This "skin" effect could play an important role under an external shock impulse induced damage because the composite material will not have enough time to develop a long wavelength geometric instability to absorb the effect of normal uniaxial shock impulse. Such a hypothetical material, if synthesized, could have useful applications in the transportation, aerospace, defense, and armor industries.

These set of simulations for nanotube mechanics have also clearly shown that in the nano-world, because of shrinking length scales and increasing accuracy of computer simulations, the simulations not only can verify and explain experimental observations but also can predict new phenomena. The phenomenon *predicted* by the quantum tight-binding molecular dynamics, such as the case of anisotropic collapse of a BN nanotube, [45] are certainly not expected to be observed in any continuum mechanics or classical MD based descriptions [15,30-31,34] because of the explicit physical and chemical nature of the atomic interactions involved. The experimentalists, in the future, might try to exploit the 'newly' predicted phenomenon such as *nanostructured skin-effect* in future development of novel light-weight high-strength and functionally smart materials.

### **3.B. Molecular Electronics: Switching and Logic with Nanotube Junctions**

The possibility of using carbon in place of silicon in the field of electronics has generated considerable enthusiasm as well. As mentioned above, the carbon nanotubes consist of rolled-up graphene sheet with various chiralities. The electronic structure of these tubes can be either metallic or semi-conducting, depending on the nature of the nanotube. The metallic and semiconducting behavior as well as the electronic transport through individual single-wall nanotubes have been extensively investigated in both theoretical and experimental studies. The main thrust has been to see if the individual (or bundles of) nanotubes could be used as quantum molecular wires for interconnects in future electronic and computing devices. The ballistic electron transport through

individual nanotubes has been supported by many independent studies, and considered to be one of the reason that nanotubes exhibit high current density as compared to other materials at the similar scale. Additionally, nanotubes have also been explored for nanoscale field effect transistors and nano-electromechanical switching devices. [46-48]

Inspired by the above, several authors have recently investigated the possibility of connecting nanotubes of different diameter and chirality, in nanotube heterojunctions, [49-52] as examples of carbon nanotube based molecular electronic devices or switching components. The simplest way to connect two dissimilar nanotubes is found to be via the introduction of pairs of heptagon and pentagon in an otherwise perfect hexagonal graphene lattice structure.[49] The resulting junction still contains three-fold coordination for all carbon atoms and the hetero-junction, between a semiconducting and a metallic nanotube, could act like a rectifying diode. Such two terminal hetero-junctions or rectifying diodes were first postulated theoretically [49-52] and recently have been observed in experiments.[53,54] The 2-terminal nanotube junctions, however, are difficult to make in experiments; much less using these in any molecular electronic circuitry for switching purposes.

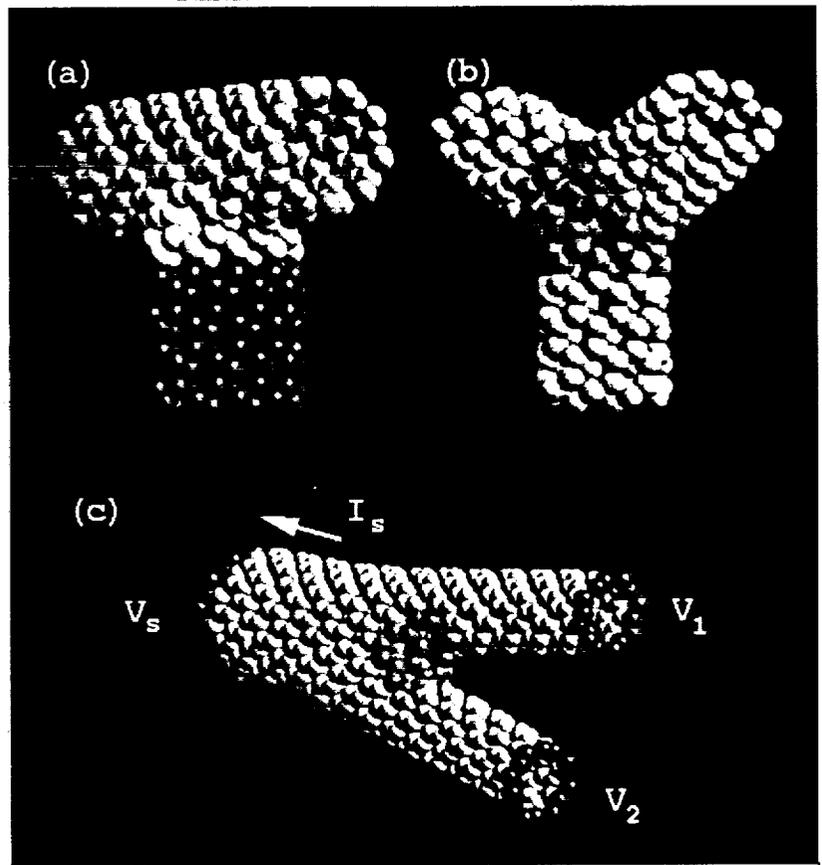
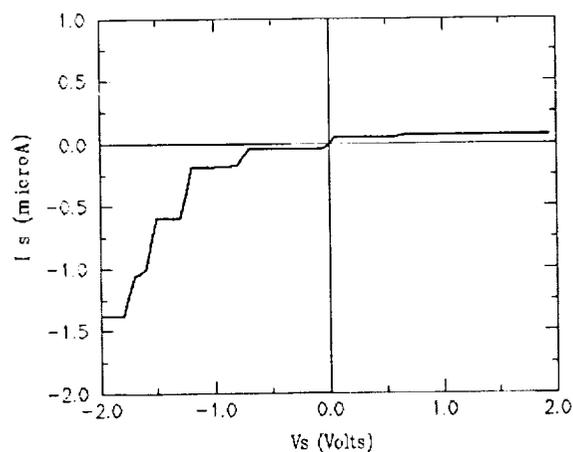


Figure 6 (a) A carbon nanotube T-junction connecting a zigzag nanotube (red) to arm chair (green) nanotube through defect rings (blue and white), (b) an obtuse angle symmetric Y-junction nanotube connecting (8,0) nanotubes in all three branches, and (c) an acute angle Y-junction connecting a (14,0) nanotube to two branches of (7,0) nanotubes.

There are two ways to go about creating more than two-terminal nanotube heterojunctions. First, connecting different nanotubes, like in the above, through molecularly perfect but topological defect mediated junctions. Second, laying down crossed nanotubes over each other and simply forming the physically contacted or touching junctions. The difference in the two approaches are the nature and characteristics of the junctions forming the device. In the first case, nanotubes are chemically connected through bonding networks forming a stable junction that could possibly give rise to a variety of switching, logic and transistor applications in the category of mono-molecular electronic or computing devices that are outlined recently an extensive review article. [55] In the second case, the junction is merely through a physical contact and will be amenable to changes in the nature of the contact. The main applications in the second category will be in electro-mechanical switches and sensors. [48] In the following we briefly describe the 'hardwired' or chemically connected junctions that were first predicted by computational nanotechnology simulations, and are now fabricated in experiments on multi-wall nanotubes.

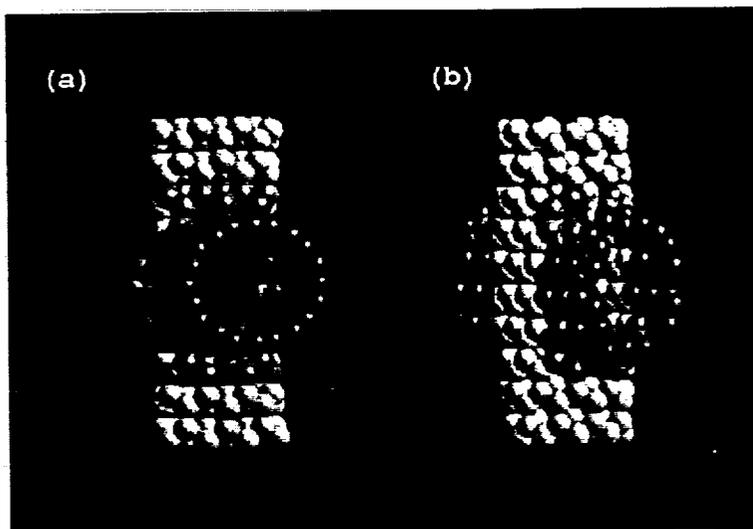
Connecting different nanotubes to form more than two terminal nanotube hetero-junctions was first proposed theoretically. [56-60] We were the first to propose the structures of a variety of carbon nanotube "T-" and "Y-junctions," as models of 3-terminal nanoscale mono-molecular electronic devices. [58-60] As prototypes of such junctions, in this article, we briefly describe "T- and "Y-junctions" formed by chemical fusing of nanotubes of different diameter and chirality at different angles to each other.[59] The initially proposed "T-junctions" can also be considered as a specific case, of a family of "Y-junctions," in which the two connecting nanotubes are perpendicular to each other. A variety of "T-junctions" are proposed and studied for electronic characterization. An example of the proposed "T-junctions" is shown in Fig. (6a). The Y-junctions pose a different kind of challenge for 3-point junction formations.[59,60] The pentagon-heptagon defect pair rule is found to be not applicable in the formation of the Y-junctions. The formation of large angle bends is explored through octagon-pentagon defect pairs. The incorporation of octagons in place of heptagons gives greater flexibility in the Y-junction formation. The number of octagonal defects equals the number of pentagonal defects in the junction region and symmetric obtuse angle Y-junctions are formed this way, and an example is shown in Fig.(6b). The electronic structure of such junctions is also explored for the basic nanoscale tunneling devices.

Progress in the recent experimental feasibility of the hardwired or chemically connected junctions has given a new thrust to this slowly expanding field of carbon nanotube based mono-molecular electronic devices. Earlier occasional experimental observations of carbon nanotube Y-junctions [61] did not attract much attention for electronics applications. This was mainly due to the difficulties associated with their synthesis and the complexities of their structures. In order for the Y-junctions to be useful from nanoscale electronic device perspective, controlled and high yield production of these junctions is required.



**Figure 7** Non-linear current-voltage characteristics in the stem S of an acute angle symmetric Y-junction of nanotubes shown in Fig. 6c.

Very recently, experimentalists have succeeded in developing template-based chemical vapor deposition (CVD), [62,63] and pyrolysis of organometallic precursor with nickelocene and thiophene, [64] techniques that allow for the reproducible and high-yield fabrication of multi-wall carbon nanotube Y-junctions. [63,64] The template based method reports junctions consisting of large diameter stems with two smaller branches with acute angle between them resembling "tuning forks" and pyrolysis method reports multiple Y-junctions along a continuous multiwall carbon nanotube. The electric conductance measurements on these Y-junctions have been performed, and show intrinsic nonlinear and asymmetric I-V behavior with rectification at room temperature.



**Figure 8** Examples of 4-terminal network junctions connecting (a) two zigzag nanotubes (green and red) of different diameters, and (b) a zigzag nanotube (green) with an armchair nanotube (red).

The structures of acute angle carbon nanotube Y-junctions are also proposed recently (Fig. 6c), and we have computed quantum conductivity of a variety of carbon nanotube Y-junctions which also show current rectification (Fig. 7) under changes in the bias voltage.[65] While all the Y-junctions considered in this work show current rectification, the degree of rectification is found to depend on the types and nature of Y-junctions considered. Some junctions show good rectification while the others show small "leakage" currents. The presence of rectification indicates, for the first time, the formation of nanoscale molecular rectifying switch with a robust behavior that is reproducible in a high-yield fabrication method. [62,63] Moreover, we also show that the molecular switches thus produced can easily function as 3-terminal bi-stable switches that are controlled by a control or "gate" voltage applied at a branch terminal. [65] In the ideal case if the gate or control terminal can be insulated from the current flowing across the junction in the other two terminals, the 3-terminal nanotube junctions such as the Y-junctions could possibly be used in standard nanoscale mono-molecular transistor or amplifier applications as well. The physical nature and the response characteristics of such devices, however, is complex and may be very different from the known standard devices so far. While the transport behavior of all Y-junctions, that we have simulated, show current rectification, the possible role of the topological defects at the junction in robustly insulating the current flow in the primary channel is not entirely clear. Charge calculations for the topological defects suggest the heptagonal rings to have positive charge. [66] The positions of the defects relative to the junction, therefore, can be expected to be a factor in rectification. The small current leakage may be attributed to the different location of heptagonal defects for different Y-junctions. Other possible reasons may also include the constructive or destructive interference of the electronic wave functions through two different channels at the location of the junction. This is further investigated by exploring the structural, or chemical potential induced, asymmetry across the two branches in a junction. The asymmetry induced rectification at the junction could be explained through complex 'self-gating' [67] effect at the junction and need to be explored in detail.

In considering the architecture for molecular electronic based devices and computing systems we need not constrain ourselves to the specifications of the silicon based devices, circuitry, and architecture. For example, one could consider an architecture of 3-dimensional network of chemically interconnected nanotubes such as with a 4-terminal nanotube junction shown in Fig. 6-8 where nodes at the junction serve as devices and switches and these are self-connected to each

other also through nanotubes. It is not easy to conceptualize, at this stage, about the possible fabrication pathways for such networks as well as the new computing or logic paradigms suitable for such network based extended architecture. A

possible alternative architecture could be based on the structure and functioning of dendritic neurons in biological neural logic and computing systems. An example of the carbon nanotube “Y-junction” based bio-mimetic dendritic neural tree is shown in Fig. 9. The tree shown in figure has 4 level of branching structure, and is made of 14 carbon nanotube “Y-junctions”. Such a structure is conceptually amenable to fabrication via template based CVD method, which is used for growing individual Y-junctions, and provides a first model



**Figure 9** An illustration of a 4-level dendritic neural tree made of 14 symmetric Y-junctions of the type described in this work.

of bio-mimetic neural network made of single or multi-wall carbon nanotubes.[68] The branching and switching of the signals at each nanotube Y-junction [Figs. 6 and 7] could be similar to what happens in a biological neural network, and once fabricated such “tree” could be trained to perform complex computing and switching applications in a single pass. The signals propagated, branched and switched on such a network also need not be restricted only to the “electronic” regime. Similar logic and switching functions may also be possible with thermal, acoustic and chemical signals. Work is currently in progress to test some of these far fetched ideas via computational nanotechnology based simulations.

### **3.C. Endo-fullerenes as Qubits for Solid-State Quantum Computer Design**

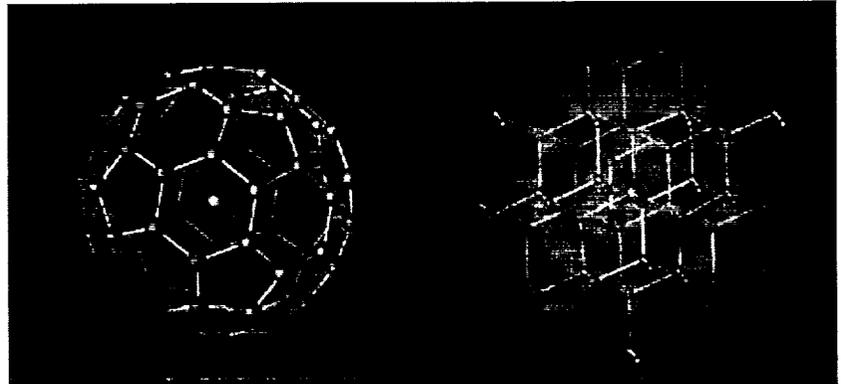
Since the development of vacuum tube electronic computer ENIAC, modern computer design has been based on sequential processing of numerical bits (zeros and ones) which forms the basis of the well-known von Neumann architecture. Quantum computation is based on a fundamentally different concept of quantum bits (qubits) which are quantum state of two level system.[69] A quantum computer with more than 20-30 qubits can outperform conventional classical computers for a certain class of computing tasks and will lead to a revolutionary increase in computing power.[70] Recent experimental demonstration of NMR quantum computation has already proved

the feasibility of a device implementation of a real quantum computer. [71,72] However, these are limited in scaling up to more than few qubit systems and would not be suitable as a platform to develop highly scalable quantum computers.

To overcome the scalability problem of NMR quantum computer, recently Bruce Kane has proposed a solid-state quantum computer based on  $^{31}\text{P}$  dopant atoms in bulk crystalline silicon. [73] In this proposal the nuclear spin of a  $^{31}\text{P}$  atom is used as a solid-state qubit. The qubit state is controlled by hyperfine coupling to the weakly bound donor electron of the  $^{31}\text{P}$  atom in Si lattice and the quantum computer can be continuously scaled using the micro fabrication technology in electronic device industry. However, there is a main challenge in realizing Kane's conceptual design of quantum computer. Experimentally, it is not known how to place a single dopant atom at a precise position in a silicon lattice and how to prevent the diffusion of the dopant atoms. Current micro fabrication technology applies  $\delta$ -doping technique to control the depth of implanted dopant atoms, but the positioning of the implanted atoms cannot be controlled with atomic precision. Furthermore, it is well known that there is significant dopant atom diffusion even at very low temperature due to the transient enhanced diffusion (TED) mechanisms (induced by silicon vacancies and self-interstitial defects).

Recently we have proposed a possible solution to these positioning and diffusion problems using the carbon based nanotechnology [74-76]. In this new design, carbon diamond lattice is proposed to replace silicon diamond lattice as a host material for  $^{31}\text{P}$  dopant atoms. This change of host material solves both positioning and stability problem as follows. The basic idea is to fabricate a diamond nanocrystallite with a  $^{31}\text{P}$  dopant atom at the center using bucky onion (multi-shell fullerenes). The sequence of fabrication steps for nanocrystallite is as follows. First, encapsulate a  $^{31}\text{P}$  atom within a  $\text{C}_{60}$  fullerene via ion implantation methods to create an endofullerene,  $\text{P@C}_{60}$ , as demonstrated in a recent experiment. [77] Second, use the  $\text{P@C}_{60}$  as a seed material to grow a bucky onion encapsulating the endofullerene. Third, use an e-beam or ion irradiation on the bucky onion to convert the inner core graphitic layers into a compressed diamond nanocrystallite. [78] Experiment has shown that the third step produces a compressed diamond nanocrystallite with 2-10 nm diameter. [78]

The position control of  $^{31}\text{P}$  atom qubit is feasible by fabricating arrays of 2-10 nm sized nanocrystallite (with  $^{31}\text{P}$  at the center) qubits in any host dielectric material including diamond lattice. The stability of the dopant atom is ensured by much higher formation energies of vacancy (7 eV) and self-interstitial ( $\sim 10$  eV) defects in diamond than those in silicon lattice. The stability of P atom is further enhanced by the stability of P atom at substitutional site relative to interstitial site (by 15 eV). Because of higher formation energies, vacancy and self-interstitial defects are not likely to form during the graphite-to-diamond transformation process



**Figure 10 (a) The stable position and valance electron charge density of a P atom in a C<sub>60</sub> fullerene, and (b) the position and weakly bound donor electron density of the P atom after it has been encapsulated in a diamond nanocrystallite.**

at the inner core of bucky onions so that the TED diffusion mechanism of P atoms will be suppressed. The Fig. 10 shows the results of *ab initio* simulations of (a) P@C<sub>60</sub> and (b) a  $^{31}\text{P}$  doped at the center of a diamond nanocrystallite. The planar valence electron density (a) and the  $^{31}\text{P}$  donor electron density in (111) plane in a diamond lattice (b) are shown in the two cases. [76] The spread of the donor electron density distribution, to define the donor electron mediated interaction between the neighboring qubits, is also estimated and will be published else where.

### 3. D. Nanotube based Sensors and Actuators:

As mentioned above, carbon nanotubes have different electronic properties depending on their chirality vector ranging from metals to semiconductors (1 eV bandgap). Semiconducting single-walled carbon nanotubes are very promising candidates for novel sensing applications since the surface modifications, due to chemical adsorption or mechanical deformation of the nanotubes, can directly modify the electronic conductance of nanotubes. Recent experimental and theoretical works have proved that single-wall nanotubes are extremely sensitive to gas molecules. [79-82]. In the experiments, the conductivity of a semiconducting nanotube shows a big change as the nanotube is exposed to miniscule amount of certain gas molecules (down to ppm level). [79,80] In the *ab initio* simulations, we have shown that the gas molecules induce charge transfer leading to

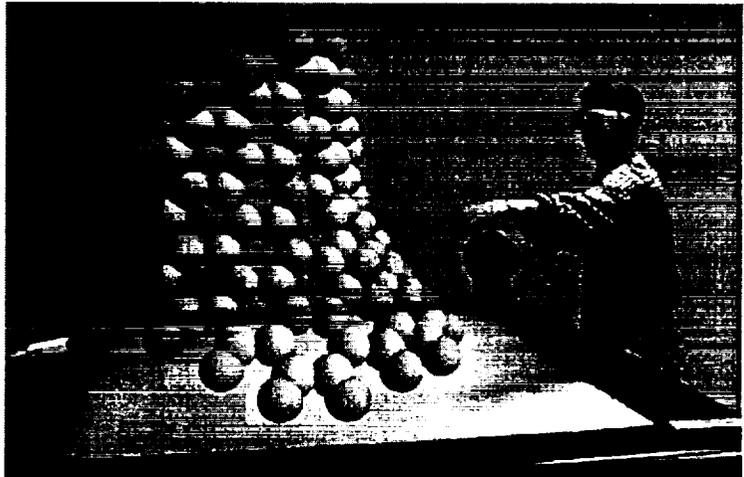
doping effects on semiconducting nanotubes. [81,83] The gas molecules (e.g., NO<sub>2</sub>) are adsorbed on the nanotube surface, and each molecule induces small amount (about 0.1 e) of electron transfer so that the nanotube becomes a p-type doped semiconductor.[79,80] Experiments have shown that the nanotube sensor can detect ppm level gas molecules at room temperature, and this opens a possibility of developing nanotube biosensor operating at physiological temperature. An *ab-initio* study of H<sub>2</sub>O adsorbed on single-wall nanotube shows a purely repulsive interaction without any charge transfer so that a SWNT can be fully immersed in water maintaining its intrinsic electronic properties. [81] Recently developed experimental technique to attach a protein on nanotube surface through non-covalent bondings shows a very promising direction to develop nanotubes for biosensor applications. [84]

Carbon nanotubes are also shown to have a strong electro-mechanical coupling in recent tight-binding [84] and *ab initio* simulations [85]. As the cross section of (8,0) SWNT is flattened up to 40%, the bandgap of the nanotube decreases from 0.57 eV and disappears at 25% deformation. As the deformation further increases to 40%, the bandgap reopens and reaches 0.45 eV. This strong dependence of SWNT band structure on the mechanical deformation can be applied to develop nanoscale mechanical sensors. Furthermore, mechanical deformation can be used to control the electronic excitation by static electric fields or electromagnetic waves. Recent *ab initio* study of polarons in SWNTs shows that the electron-hole pair creation can induce a tube length change leading to optical actuation mechanism of nanotube mechanical properties [86]. The strong coupling of electronic, optical, and mechanical properties of SWNT offers a great opportunity to develop novel nanodevices which can be controlled and actuated by E&M waves as shown by a recent experimental demonstration [87].

#### **4. Molecular Machines and Building the World with Bottom Up Technology**

The above examples provide a narrow window on a very broad field of applications and areas that are possible and are directly fuelled by the efforts and advances in the computational nanotechnology. From materials to electronics, to computers and machines, in fact could provide components of probably functional molecular scale machines or robots (nanobots) in future. Much of the recent progress in this field is in the experimental bio-molecular motors arena where not only significant understanding has been made about how the natural biological motor systems work, but

also of creating interfaces of nanoscale bio-molecular motors with synthetic materials in solution phase environments.[88,89] Means to power these machines through biomimetic physical and chemical phenomenon are also under investigation. Ultimately, one can probably conceptualize nanoscale synthetic machines and motors, which could be powered and controlled through external laser, electric or magnetic fields and which could operate in chemical solution phase or inert gas environment. The computational nanotechnology team at NASA Ames conceptualized carbon naotube based gears [90] and how to power those gears through external laser fields [91,92]. The design of the gears were based on chemical reactions that are known to occur, though, no fabrication pathway for making such nanoscale gears has been suggested. Optimal operating conditions were investigated and the main finding was that such gears, if made, could be more robust than similar gears and other machines fabricated and operated in the macro-world.



**Figure 11 Illustration of a working VMS simulator at NASA Ames where building blocks of materials, with reactions described by classical MD, can be brought together with an haptic interface in real time to check the possibility of synthesis of 'new' materials and devices.**

Lastly comes the question of building the world through 'atom by atom' assembly from the bottom up – the holy grail of - molecular technology. Experimentally, there are areas that could contribute significantly towards the advances in this direction. These areas are nanomanipulation and control of atomic and molecular level entities on solid surfaces and in three dimension, as well as self-assembly of molecular scale materials where chemical and topological structural forces can guide chunks of nanoscale materials towards larger functional materials structures. Computational nanotechnology does and can contribute significantly, towards this direction, by possibly simulating the assembly of the building blocks of materials and systems in a virtual reality based nano-manipulation and synthesis simulators. Interestingly, real progress has been made in developing both experiments and simulations of these technologies: experimental nanomanipulators control real time manipulation, [93,94] and Virtual Mechano-synthesis (VMS)

simulator [95] at NASA Ames (Fig. 11) can bring together nanoscale chunks of materials in a virtual reality simulator to come up with nanotube junctions and interfaces that are otherwise difficult to visualize in reality.

#### ACKNOWLEDGEMENTS:

Part of this work (DS) is supported by NASA contract 704-40-32 to CSC. The author (MM) is supported through grants by NSF (MRSEC Program under award number DMR-9809686), DEPSCoR (99-63231 and 99-63232), DOE Grant (00-63857), NASA grant (00-64338) and the University of Kentucky Center for Computational Sciences. The *ab-initio* The DFT simulations were performed under the NPACI allocation SUA239 "Nanoscale Materials Simulations."

#### REFERENCES:

- [1] S. Iijima, *Nature*, **354**, 56 (1991)
- [2] S. Iijima and T. Ichihashi, *Nature*, **363**, 603 (1993)
- [3] D.S. Bethune, C.-H. Kiang, M.S. deVries, G. Gorman, R. Savoy, J. Vazquez, and R. Beyers, *Nature* **363**, 605 (1993)
- [4] See for example R. Saito, G. Dresselhaus and M. S. Dresselhaus, *Physical Properties of Carbon nanotubes*, (Imperial College Press, London 1998) and references there in; *Fullerene Nanotubes: C1,000,000 and Beyond*, B.I.Yakobson and R.E.Smalley, *American Scientist* **85**, 324-337, (1997)
- [5] M. S. Daw and M. I. Baskes, *Phys. Rev. Lett.* **50**, 1285 (1983); S. M. Foiles, M. I. Baskes, and M. S. Daw, *Phys. Rev.* **B33**, 7983 (1986)
- [6] F. H. Stillinger and T. A. Weber, *Phys. Rev.* **B31**, 5262 (1985)
- [7] J. Tersoff, *Phys. Rev.* **B38**, 9902 (1988)
- [8] D. W. Brenner, *Phys. Rev.* **B42**, 9458 (1990)
- [9] B. J. Garrison and D. Srivastava, *Ann. Rev. Phys. Chem.* **46**, 373 (1995)
- [10] R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).
- [11] W. A. Harrison, *Electronic Structure and the Properties of Solids*, (Freeman, San Francisco, 1980)
- [12] Payne et al., *Rev. Mod. Phys.* **68**, 1045 (1992) for a detailed review.
- [13] See for example methodology and references in; S.Datta, *Electronic Transport in Mesoscopic Systems*, (Cambridge Univ. Press, Cambridge 1995)
- [14] See for example M. P. Allen and D. J. Tildesley, *Computer Simulations of Liquids*, (Oxford: Oxford Science Publications 1997); and D.C.Rapaport, *The Art of Molecular Dynamics Simulation*, (Cambridge Univ. Press, Cambridge 1995)
- [15] D. Srivastava and S. Barnard, in *Proceedings of IEEE Supercomputing '97 (SC '97)* (1997)
- [16] M. van Schilfgaarde and W. A. Harrison, *Phys. Rev.* **B33**, 2653 (1986)
- [17] M. Menon, E. Richter and K. R. Subbaswamy, *J. Chem. Phys.* **104**, 5875 (1996)
- [18] M. Menon and K.R. Subbaswamy, *Phys. Rev.* **B55**, 9231 (1997)
- [19] J. Ihm, *Rep. Prog. Phys.* **51**, 105 (1988); W.E. Pickett, *Comp. Phys. Rep* **9**, 115 (1989)
- [20] P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, 864B (1964)

- [21] W. Kohn and L.J. Sham, Phys. Rev. **140**, 1133A (1965)
- [22] Check the web site for the details, <http://cms.mpi.univie.ac.at/vasp/>
- [23] Ismail Beigi S, Arias TA, Comp. Phys. Comm. **128**, 1 (2000)
- [24] R.Landauer, Z.Phys. **B68**, 217 (1987).
- [25] A. N. Andriotis, M. Menon and G. E. Froudakis, Phys. Rev. Lett. **85**, 3193 (2000);  
A. N. Andriotis and M. Menon, Phys. Rev. Phys. Rev. **B60**, 4521 (1999)
- [26] A.N.Andriotis and M.Menon, submitted for publication (2001)
- [27] J. E. Inglesfield, J. Phys. C**14**, 3795 (1981)
- [28] A. J. Fisher, J. Phys. Condens. Matter **2**, 6079 (1990)
- [29] N. D. Lang and Ph. Avouris, Phys. Rev. Lett. **84**, 358 (2000)
- [30] B. I. Yakobson, C.J. Brabec and J. Bernholc, Phys. Rev. Lett. **76**, 2511 (1996)
- [31] J. Bernholc, C.Brabec, M. Buongioron, A. Maiti, B.I. Yakobson, Appl. Phys. A**67**, 39, (1998)
- [32] D. Srivastava, M. Menon and K. Cho, Phys. Rev. Lett. **83**, 2973 (1999)
- [33] T. Ozaki, Y, Iwasa and T. Mitani, Phys. Rev. Lett. **84** (2000)
- [34] B.I.Yakobson and Ph.Avouris, "*Mechanical Properties of Carbon Nanotubes,*"  
Carbon Nanotubes, Eds. M.S.Dresselhaus and Ph.Avouris 293 (Springer  
Verlag, Berlin-Heidelberg, 2001)
- [35] L.S. Schadler, S.C. Giannaris, and P.M. Ajayan, Appl. Phys. Lett. **73**, 3842 (1998)
- [36] O. Lourie, D. M. Cox and H. D. Wagner, Phys. Rev. Lett. **81**, 1638 (1998)
- [37] R. Andrews, D. Jacques, A.M. Rao, T. Rantell, F. Derbyshire, Y. Chen, J. Chen and  
R.C. Haddon, Appl. Phys. Lett. **75**, 1329 (1999)
- [38] D. Qian, E.C. Dickey, R. Andrews and T. Rantell, Appl. Phys. Lett. **76**, 2868 (2000)
- [39] F. Banhart and P. M. Ajayan, Nature **382**, 433 (1996)
- [40] X. Blase, A. D. Vita, J.-C. Charlier and R. Car, Phys. Rev. Lett. **80**, 1666 (1998)
- [41] E. Hernandez, C. Goze, P. Bernier, and A. Rubio Phys. Rev. Lett. **80**, 4502 (1998)
- [42] M. Menon and D. Srivastava, Chem. Phys. Lett. **307**, 407 (1999)
- [43] D. Goldberg, Y. Bando, K. Kurashima, T. Sato, Solid State Comm. **116**, 1 (2000)
- [44] D. Goldberg, Y bando, L. Bourgeois, K. Kurashima and T. Sato, Appl. Phys. Lett.  
**77** 1979 (2000)
- [45] D. Srivastava, M. Menon and K. Cho, Phys. Rev. B, to appear (15 April 2001)
- [46] See for example; C. Dekker, Physics Today **52**, 22(1999); L. C. Venema and C. Dekker,  
*New Frontiers of Science and Technology*, ed. L. Esaki, pg 293 (Frontier Science Sr. No. 31  
Universal Academic Press 2000)
- [47] See for examples; P. Collins and P. Avouris, Scientific American, pg. 62 (Dec. 2000)
- [48] T. Rueckes, K. Kim, E. Joselevich, G. Y. Tseng, C-L Cheung, C. M. Lieber, Science  
**289**, 94 (2000)
- [49] L. Chico, V. H. Crespi, L. X. Benedict, S. G. Louie, and M. L. Cohen, Phys. Rev. Lett.  
**76**, 971 (1996)
- [50] J. C. Charlier, T. W. Ebbesen, and Ph. Lambin, Phys. Rev. **B53**, 11108 (1996)
- [51] R. Saito, G. Dresselhaus and M. S. Dresselhaus, Phys. Rev. B **53**, 2044 (1996)
- [52] M. Menon, D. Srivastava and S. Saini, *Second NASA Device Modeling Workshop*,  
NASA Ames, Moffet Field, California 1997
- [53] J. Han, M. P. Anantram, R. Jaffe, and H. Dai, Phys. Rev. **B57**, 14983 (1998)
- [54] Z. Yao, H. W. C. Postma, L. Balants, and C. Dekker, Nature **402**, 273 (1999)
- [55] C. Joachim, J. K. Gimzewski and A. Aviram, Nature **408**, 541 (2000)
- [56] L. A. Chernozatonskii, Phys. Lett. A **172**, 173 (1992)

- [57] G.E.Scuseria, Chem. Phys. Lett. **195**, 534 (1992)
- [58] M. Menon and D. Srivastava, Phys. Rev. Lett. **79**, 4453 (1997)
- [59] M. Menon and D. Srivastava, J. Mat. Res. **13**, 2357 (1998)
- [60] D. Srivastava, S. Saini and M. Menon, "Molecular Electronics: Science and Technology," ed A. Aviram and M. Ratner, Annals of New York Academy of Sciences **852**, 178 (1998)
- [61] D.Zhou and S.Seraphin, Chem. Phys. Lett. **238**, 286 (1995)
- [62] J.Li, C.Papadopoulos and J.Xu, Nature **402**, 253 (1999)
- [63] C.Papadopoulos, A.Rakitin, J.Li, A.S.Vedeneev and J.M.Xu, Phys. Rev. Lett. **85**, 3476 (2000)
- [64] C. Satishkumar, P. J. Thomas, A. Govindraj, and C. N. R. Rao, Appl. Phys. Lett. **77**, 2530 (2000)
- [65] A. Antonis, M. Menon, D. Srivastava, G. Froudakis and L. A. Chernozatonskii, submitted, Phys. Rev. Lett. (2001)
- [66] R. Tamura and M. Tsukada, Phys. Rev. **B49**, 7697 (1994)
- [67] J-O J. Westrom, Phys. Rev. Lett. **82**, 2564 (1999)
- [68] D. Srivastava, Unpublished (2001)
- [69] See the theme articles on quantum computation, *Computing in Science & Technology* (March/April 2001)
- [70] S.K. Moore, IEEE SPECTRUM, pp. 18-19 (Oct. 2000)
- [71] N. A. Gershenfeld and I. L. Chuang, Science **275**, 350 (1997)
- [72] I. L. Chuang, L. M. K. Vandersypen, X. L. Zhou, D. W. Leung and S. Lloyd, Nature **393**, 143 (1998)
- [73] B. E. Kane, Nature **393**, 133 (1998)
- [74] D. Srivastava, T. R. Govindan and K. Cho, NASA Ames DDF Proposal Award (1999)
- [75] S. Park, D. Srivastava and K. Cho, Special Issue of Journal Nanotechnology, submitted (2000)
- [76] S. Park, D. Srivastava, and K. Cho, J. Nanoscience and Nanotechnology, submitted (2001)
- [77] C. Knapp et. al. Molecular Physics **95**, 999 (1998)
- [78] F. J. Banhart, J. Appl. Phys. **81**, 3440-3445 (1997)
- [79] J.Kong, N.R. Franklin, C.Zhou, M.G. Chapline, S. Peng, K.J. Cho and H. Dai, Science **287**, 622 (2000)
- [80] P.G. Collins, K. Bradley, M. Ishigami, and A. Zettl, Science **287**, 1801 (2000)
- [81] S. Peng and K.J. Cho, Nanotechnology **11**, 57 (2000)
- [82] S. Jhi, S.G. Louie, and M.L. Cohen, Phys. Rev. Lett. **85**, pp. 1710-1713 (2000)
- [83] P. Shu and K. Cho, submitted (2001)
- [84] H. Dai (private communications)
- [85] L. Yang and J. Han, Phys. Rev. Lett. (2000)
- [86] M. Verissimo-Alves et al., Phys. Rev. Lett. (in press) (2001)
- [87] Y. Zhang and S. Iijima, Phys. Rev. Lett. **82**, 3472 (1999)
- [88] See for example C. Montemagno and G. Bachand, Nanotechnology **10**, 225 (1999)
- [89] J. R. Dennis, H. Howard and V. Vogle, Nanotechnology **10**, 232 (1999)
- [90] J. Han, A. Globus, R. Jaffe and G. Deardorff, Nanotechnology **8**, 95 (1997)
- [91] D. Srivastava, Nanotechnology **8**, 186 (1997)
- [92] Animations are available at: <http://www.nas.nasa.gov/Groups/SciTech/nano/index.html>
- [93] See for Example: R. M. Taylor II and R. Superfine, "Advance Interfaces to Scanning Probe Microscopes," in Handbook of Nanostructured Materials and Nanotechnology, Ed. H. S. Nalwa, Ed., (Academic Press, New York 1999)
- [94] M F Yu, M. J. Dayer, G. D. Skidmore, H. W. Rohrs, X. K. Lu, K. D. Ausman, J. V. Ehr,